PennState

# Multifunctional Lithium-Ion Conducting Interfacial Materials for Lithium-Metal Batteries

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**Project ID: BAT445**

# Overview

## Timeline

- Project start date: April 01, 2019.
- Project end date: March 31, 2021
- Percent complete: 40%

## Barriers

- Protective layers for Li metal anode
  - Thin, dense and uniform protective coating
  - Stable to over wide voltage range
  - Scalable and compatible with pouch cell

## Budget

- Total project funding
  - DOE share: $800K
  - Contractor share: $90K
- Funding received in FY 2020
  - DOE share: $450,327
  - Contractor share: $45,000

## Partners

- Project lead
  - PSU
- Interactions/collaborations
  - Ashland

# Relevance

## Objectives

- To research, develop, and demonstrate multifunctional Li-ion conducting interfacial materials as a protective layer for Li metal anodes, enabling Li metal anodes to cycle with a high efficiency of ~99.9% at a high electrode capacity (4 $mAh/cm^2$) and a high current density (>2 $mA/cm^2$) for 400 cycles.
- Demonstrate Li-metal battery cells with an energy density of ~300 Wh/kg and a ≥80% capacity retention over 300 cycles using Li metal anodes with the developed protective layer.

## Impacts

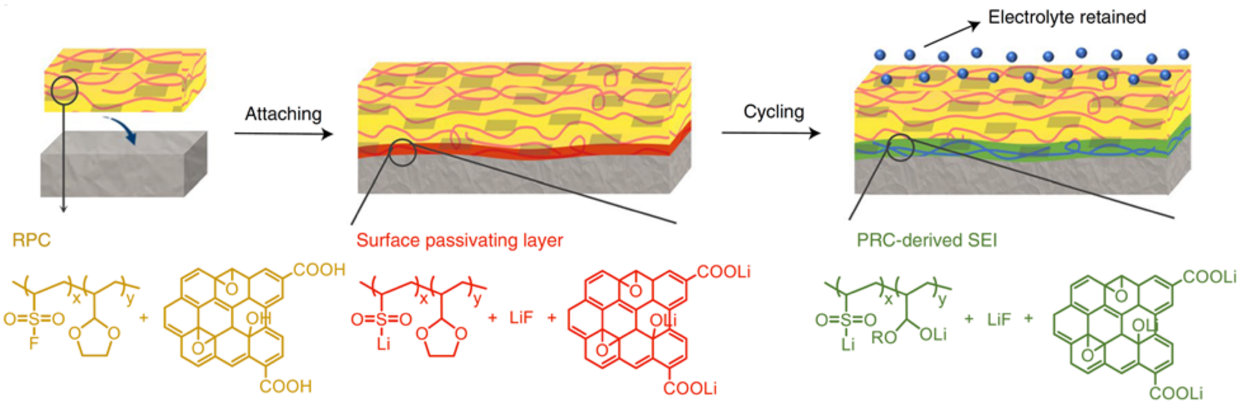
- Develop a new hybrid Li-ion conductor that enables safe and high-performance Li metal anodes.
- The use of the developed Li metal anodes enable Li-metal oxide batteries with high energy density and long cycling life.
- Promote increased adoption of electric and plug-in hybrid electric vehicles (EVs and PHEVs), and reduce petroleum consumption in the transportation sector by helping battery-powered vehicles become accepted by consumers as a reliable source of transportation

# Milestones

| Date | Milestones | Status |
|---|---|---|
| Sep. 2019 | Identify the optimal composition of the Li-ion conducting materials and demonstrate Li metal batteries under high-capacity (4 $mAh/cm^2$) and lean-electrolyte (7 $\mu L/mAh$) conditions. | Complete |
| Mar. 2020 | Complete the scale-up synthesis of the interfacial layer precursors | Complete |
| Jul. 2020 | Study the effects of the interfacial layer on the lithium nucleation | In progress |
| Jan. 2021 | Develop protected Li anodes using optimal electrolyte, which have 99.9% CE of Li deposition at a capacity of 4 $mAh/cm^2$ | On track |
| Mar. 2021 | Demonstrate Li metal batteries with a cycle life of 100 cycles under limited Li and lean-electrolyte conditions. | On track |

# Approach

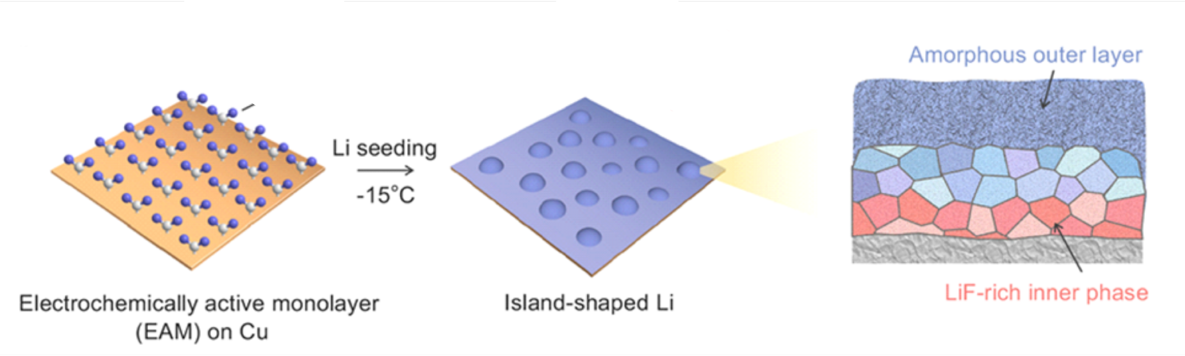
I




**Li metal protection**

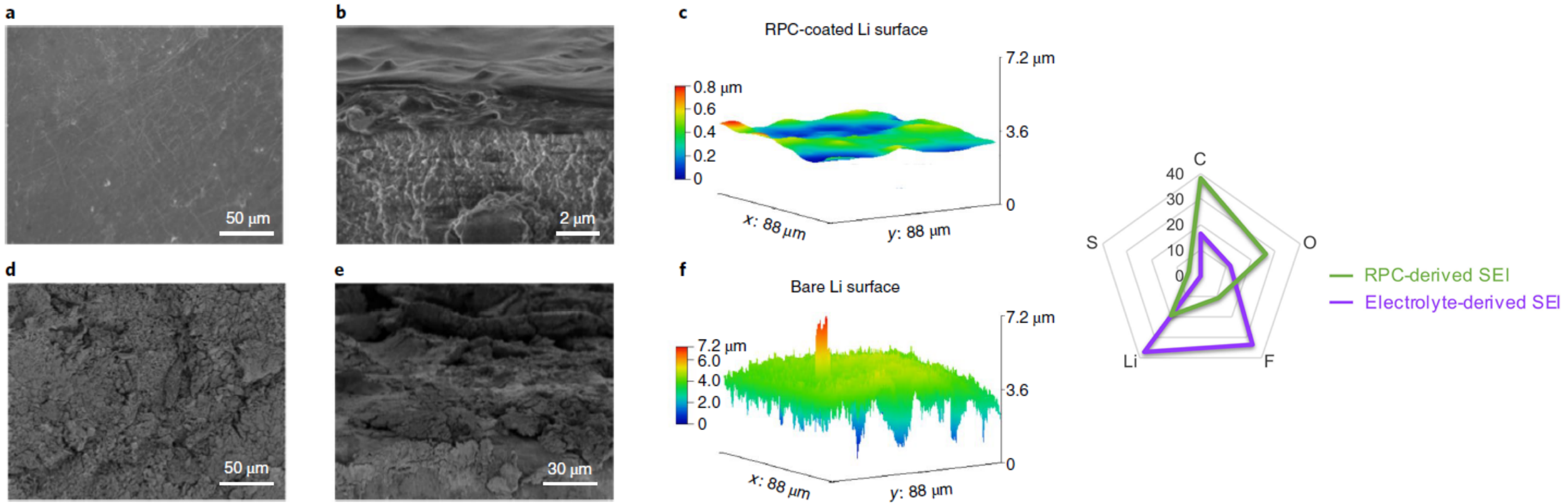
A bottom-up design using a **reactive polymer composite (RPC)**, can enables excellent cycling performance under lean electrolyte, limited Li excess and high capacity conditions.

II




An **electrochemically active monolayer (EAM)** strategy can efficiently improve the Li metal battery performance **at low temperature (-15 °C)**.

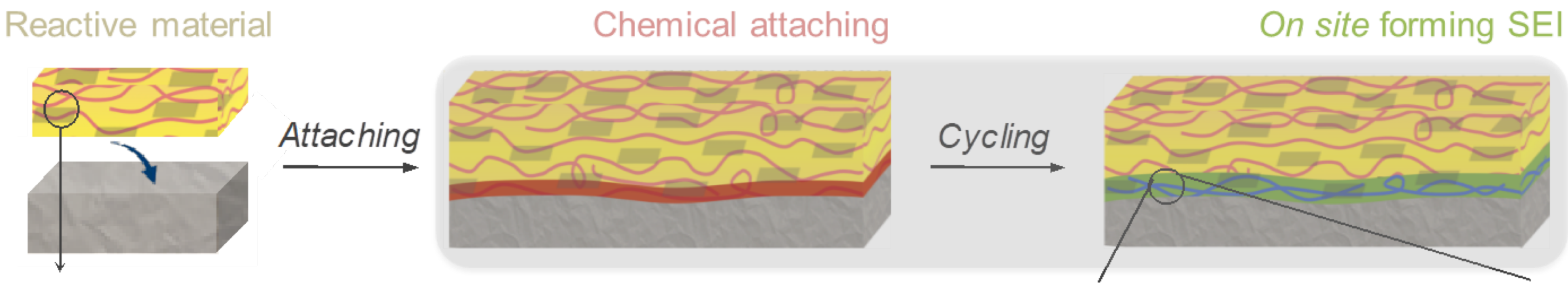
# Technical Accomplishment - 1. Bottom-up design of multifunctional Li-ion conducting interfacial materials

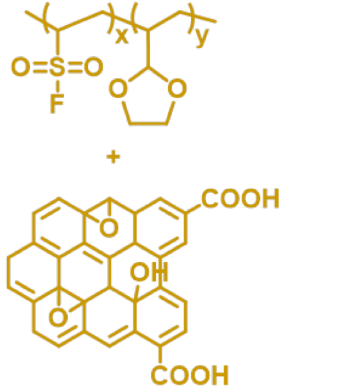



Thin RPC-derived SEI, distinct from conventional electrolyte-derived SEI, enables uniform Li deposition upon long cycling. Stable cycling (over 200 cycles) of a 4 V Li|NCM523 battery cell was achieved under lean electrolyte (7 µl $mAh^{-1}$), limited Li excess (1.9-fold excess of Li) and high areal capacity (3.4 mAh $cm^{-2}$)

*Nat. Mater.* **2019**, 18 (4), 384-389.

# SEI regulated by the RPC composite



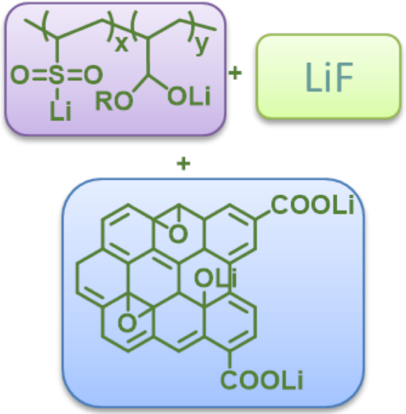




graphene oxide (GO)

RPC

**Advantage of RPC:**

1. Dense (polymer-nanoparticle)
2. Passive (LiF)
3. Homogeneous (*on site* forming)
4. Mechanically strong (GO)




RPC-derived SEI

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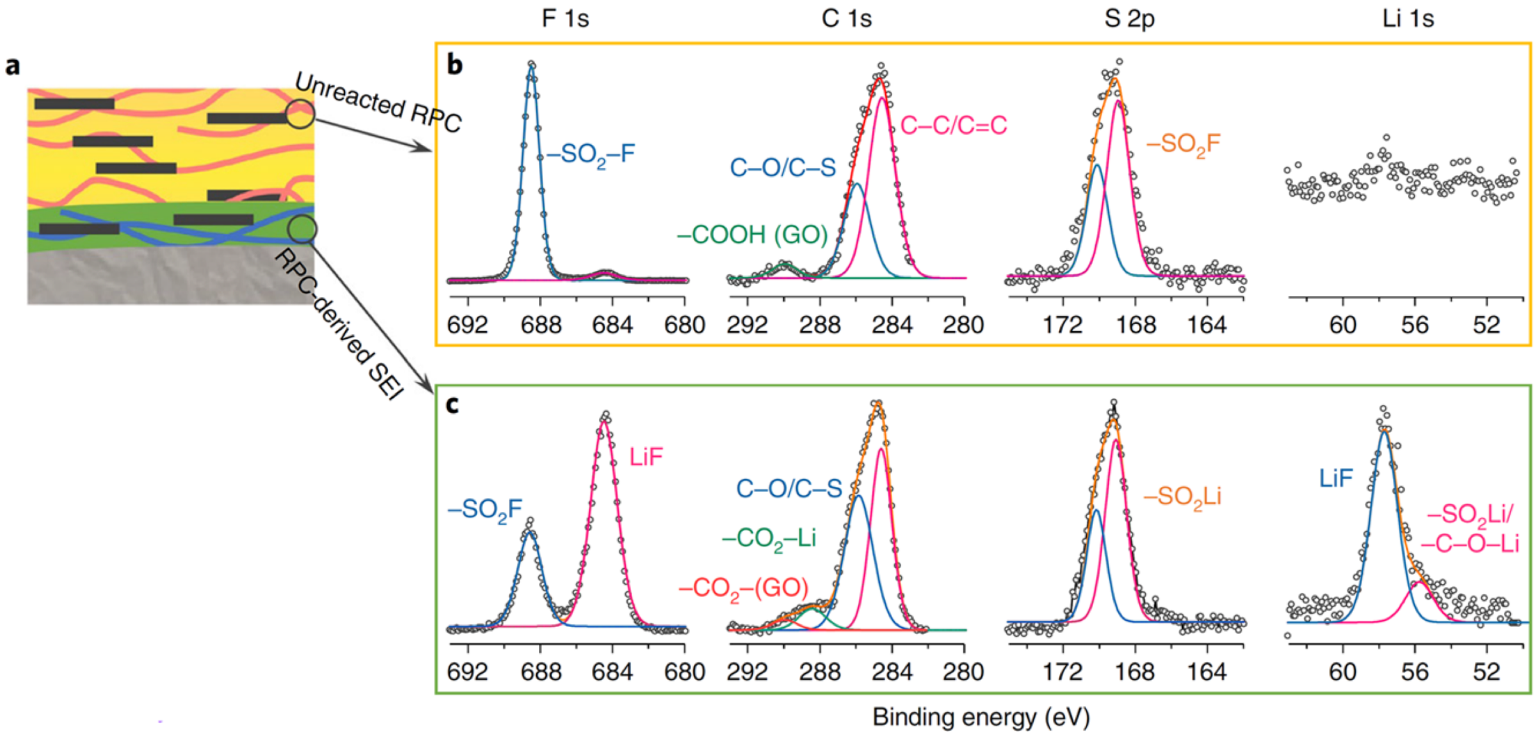
# SEI Chemistry ruled by the RPC composite




The lamellar composite provides excellent SEI stability on cycling.
The unreacted RPC serves as a reservoir to maintain the SEI on cycling.

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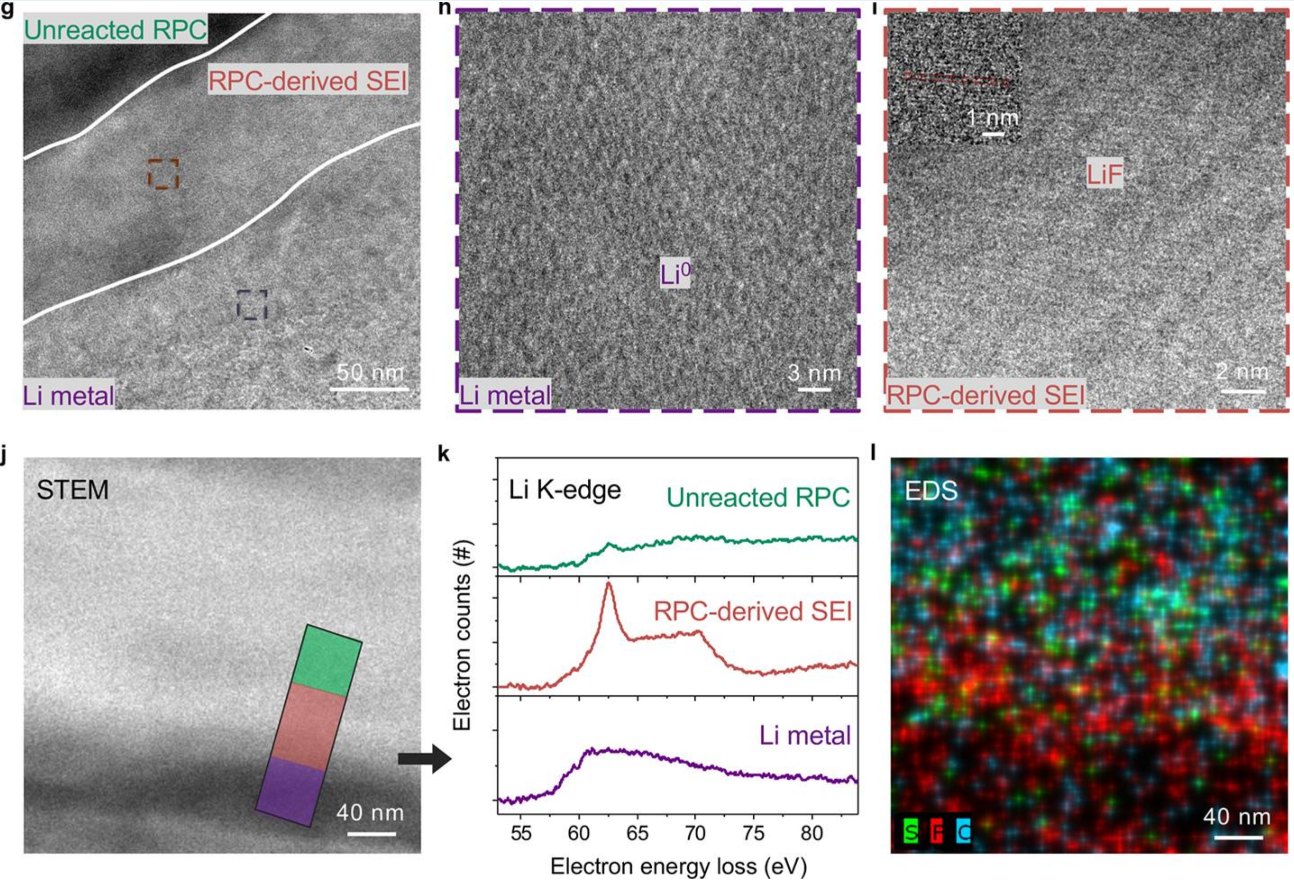
# Nanostructure of the RPC-derived SEI




Three layers:
unreacted RPC,
RPC-derived SEI (~90-120 nm) and Li.

**RPC-derived SEI:**
**Amorphous, homogeneous and dense**.
(The keys for the improved SEI stability and effective suppression of dendritic Li growth)

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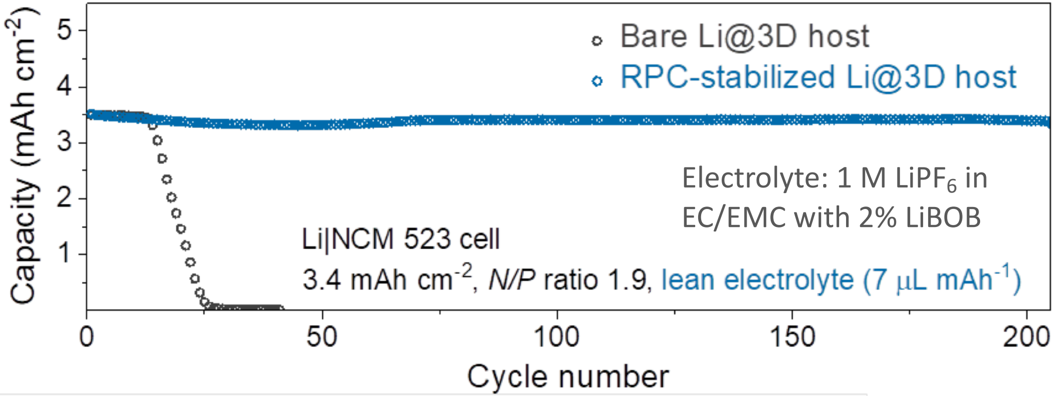
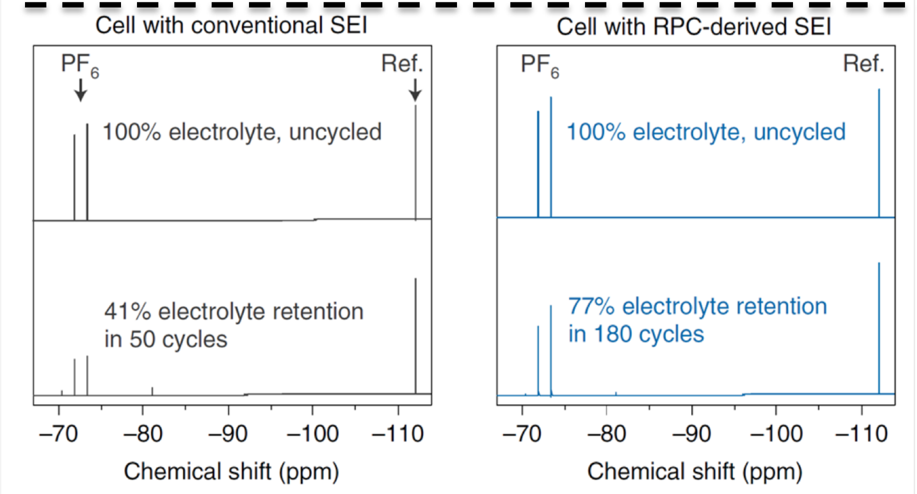
# Electrochemical performance of RPC-stabilized Li metal batteries




At a N/P ratio of 1.9, stable cycling performance over 200 cycles with a capacity retention of 90.7% in the Li|NCM523 cell with areal capacity of 3.4 mAh cm$^{-2}$ under lean electrolyte.




The polymer–inorganic structure of the RPC-derived SEI confers good stability and effective suppression of electrolyte decomposition based on the NMR studies.

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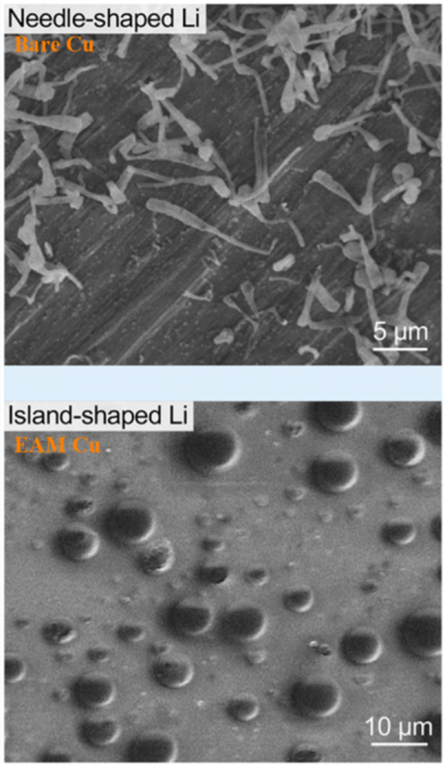
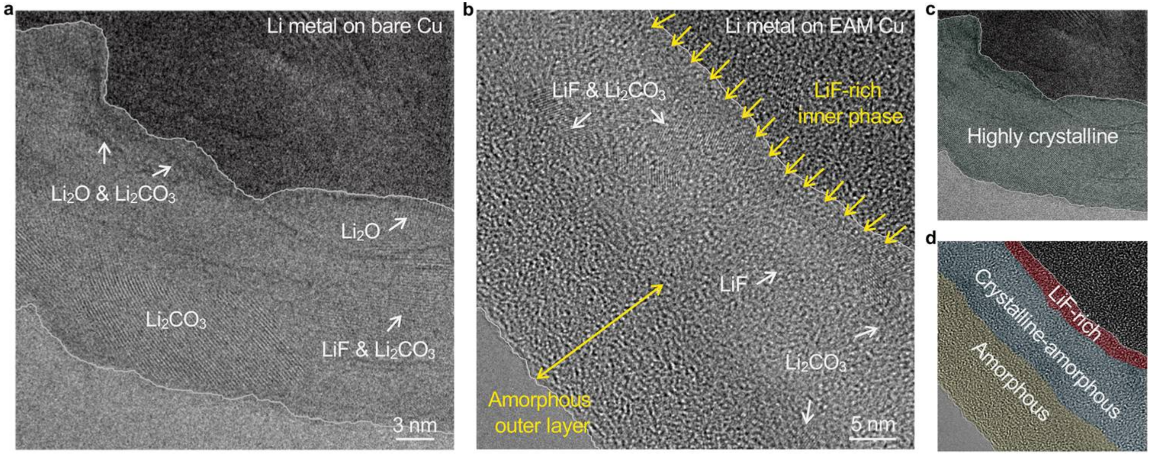
# Technical Accomplishment - 2. Low-temperature (-15 °C) Li anode SEI



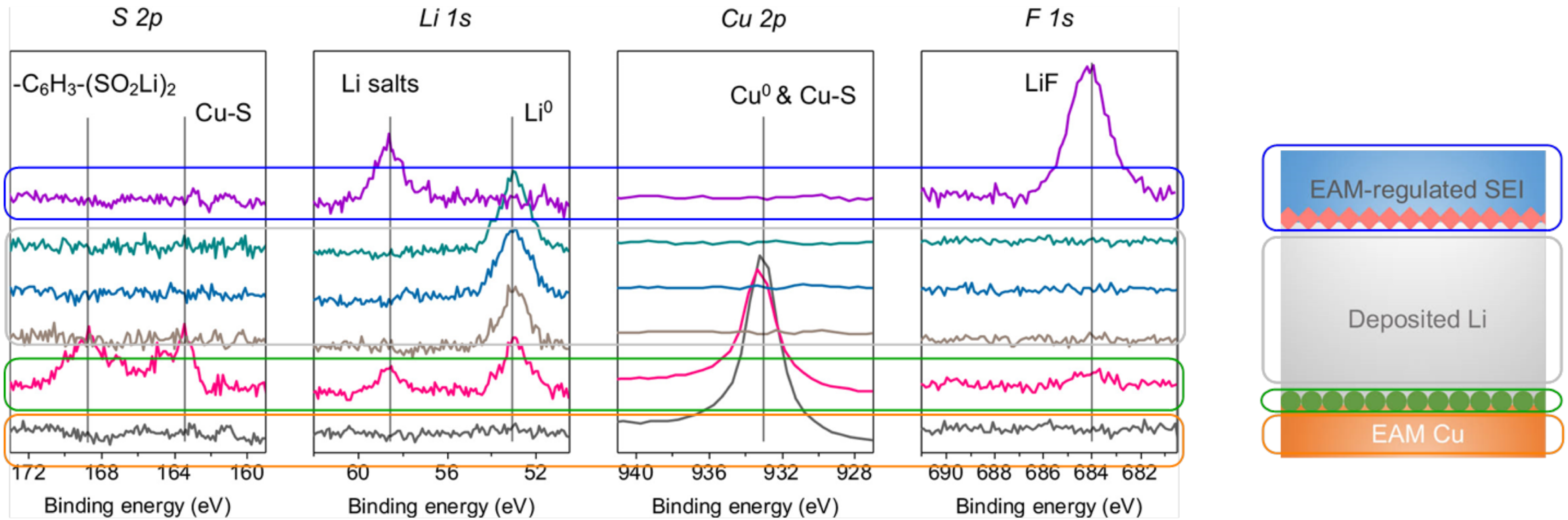

At -15 $^{o}$C, 6 mA cm$^{-2}$ & 6 mAh cm$^{-2}$

The EAM Cu enables the island-shaped Li deposition.




The electrochemically active EAM modification on Cu providing the LiF-rich inner phase and amorphous outer layer, can efficiently improve the cycling performance of Li metal batteries at -15 $^{o}$C.

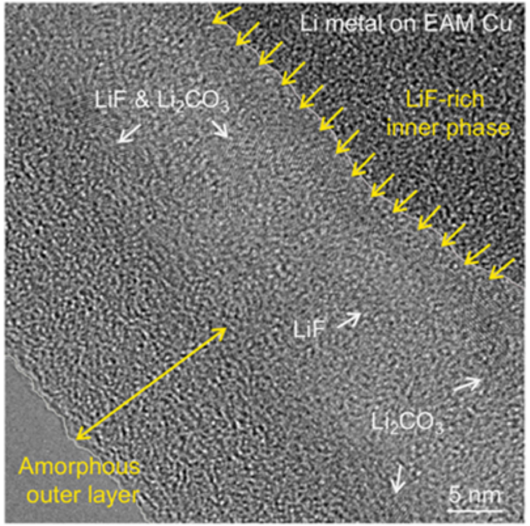
# Interface chemistry in the presence of EAM



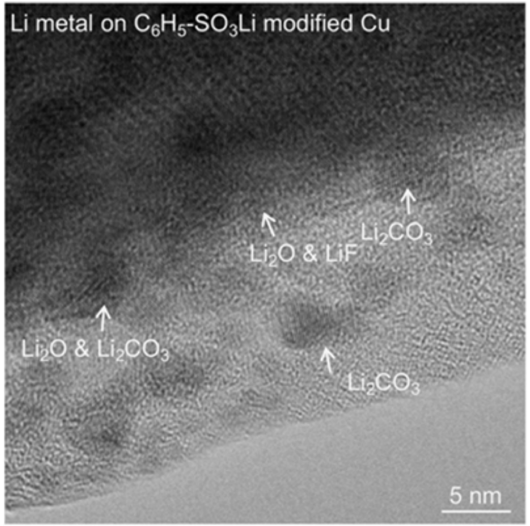

The sulfonyl fluoride group of EAM provides LiF-rich layer at the top of deposited Li, along with the formation of $–SO_2Li$ salts at the interface between the Cu substrate and deposited Li.

# SEI Nanostructure regulated by EAM

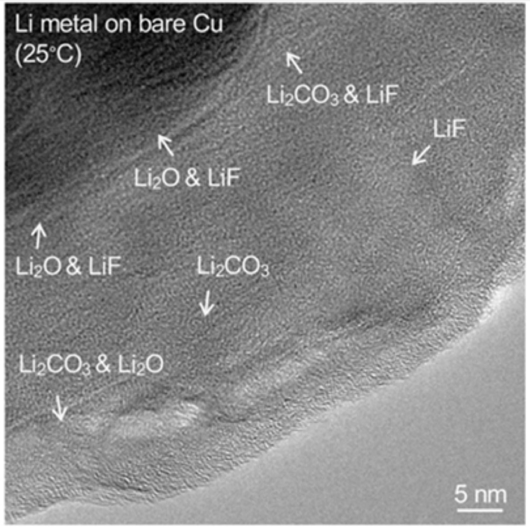
Active, EAM Cu, -15°C




Inactive, without LiF generation




Bare Cu, 25°C

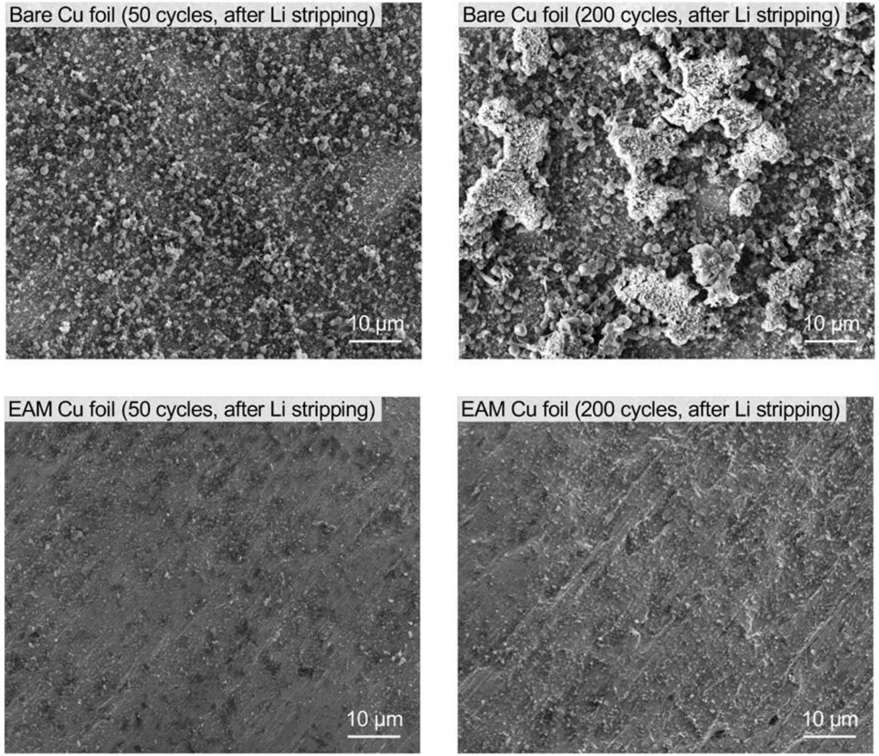



Electrolyte: 1M $LiPF_6$ in PC/FEC (8:1)

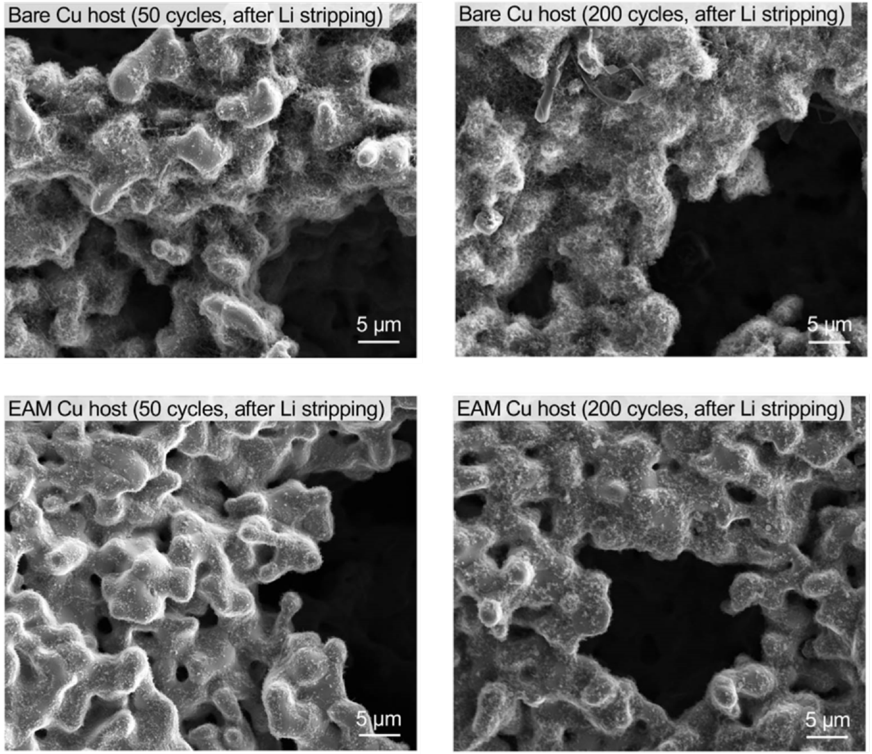
Uniform and dense inner LiF-rich phase and amorphous outer layer are formed at low temperature (-15 $^oC$), while the electrochemically inactive modification and bare Cu result in incompact and non-uniform interface.

# Stable interface enabled by EAM

**2D Cu surface after cycling**

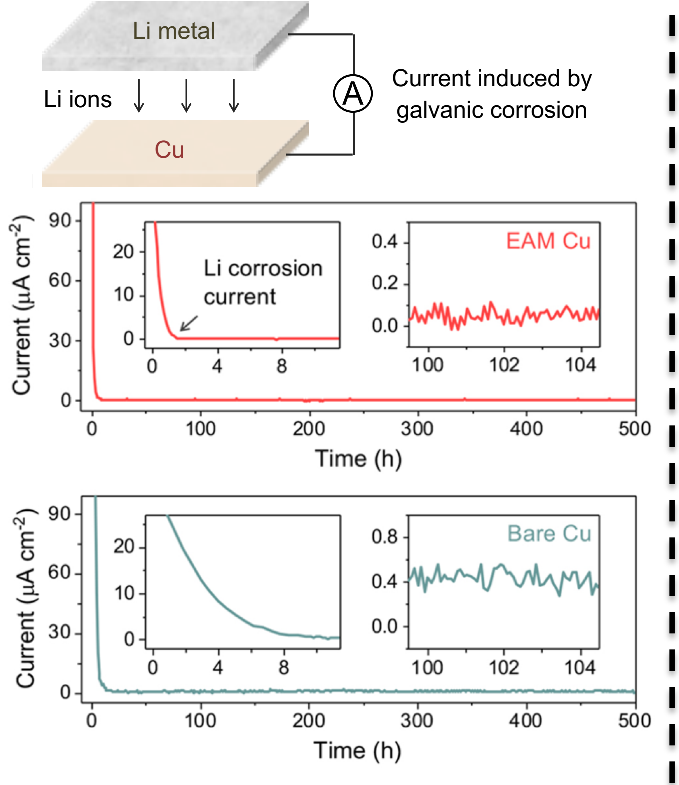



**3D Cu surface after cycling**

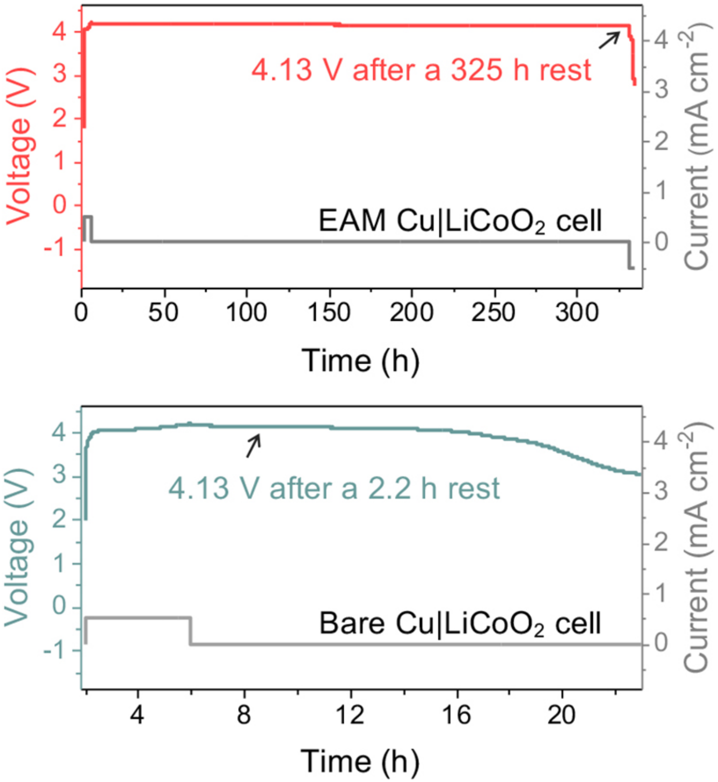



The EAM 2D/3D Cu provided clean surface over 200 cycles, however, the bare Cu resulted in dead Li and waste SEI.

# Restrained galvanic corrosion and surface self-discharge by EAM

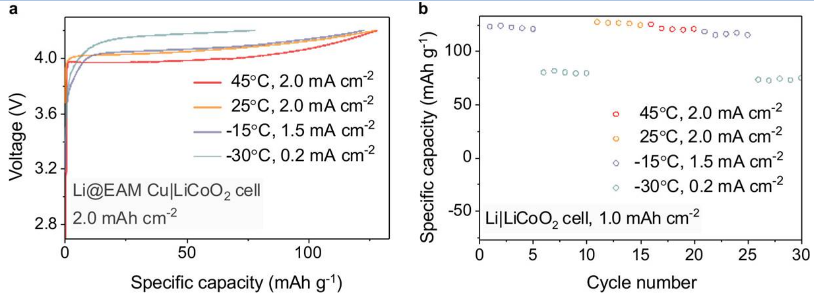



Significantly reduced Li corrosion by EAM Cu

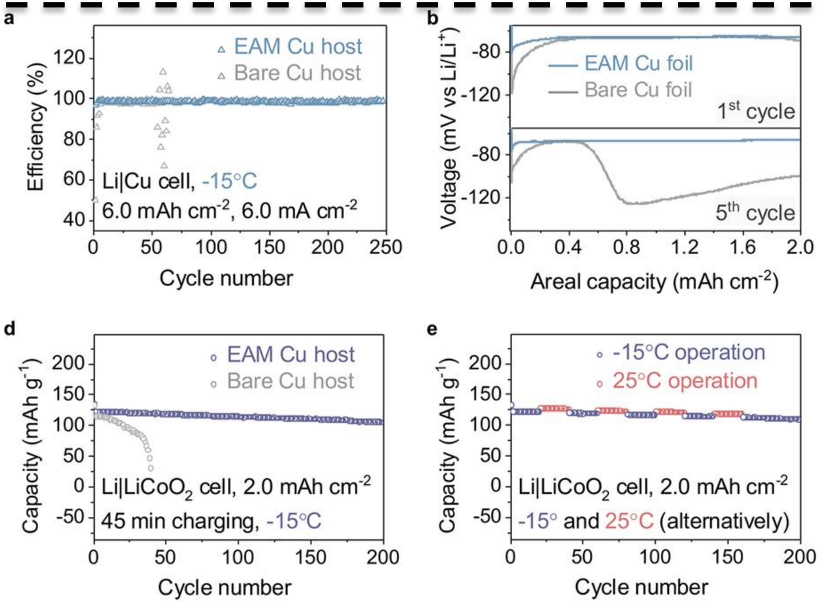



Efficiently restrained self-discharge of anode-free Li|$LiCoO_2$ cells

# Electrochemical performance enhanced by EAM




The Li@EAM Cu anodes provide wide temperature window (-30—45 $^{o}$C).




At low temperature (-15 $^{o}$C) the Li@EAM Cu anodes demonstrates dramatically improved cycling performance, which is comparative to the performance at 25 $^{o}$C.

# Responses to Previous Year Comments

**The project was not reviewed last year.**

# Partners/Collaborators

- Collaboration with Dr. Alan Goliaszewski at Ashland Specialty Ingredients G.P. on the scale-up fabrication of the Li-ion conducting polymer.

- Collaboration with Dr. Ji-Guang Zhang at PNNL on fabrication and testing of Li metal batteries with the protective layers.

- Collaboration with Dr. Anh Ngo on computational modeling from Argonne National Lab.

# Remaining Challenges and Barriers

- Further optimize the synthesis of multifunctional Li-ion conducting interfacial materials with cheaper and readily available precursors.
- Completely suppressing the Li dendrite upon long cycling.
- Application of the protective Li metal anodes under higher specific capacity for promising practical application under lean electrolyte.

# Proposed Future Work

| | |
|---|---|
| **Ongoing (FY20 and FY21)** | Study the effects of the interfacial layer on the lithium nucleation. (In progress, July 2020) |
| | Develop protected Li anodes using optimal electrolyte, which have 99.9% CE of Li deposition at a capacity of 4 $mAh/cm^2$ (Oct. 2020) |
| | Demonstrate Li metal batteries with a cycle life of 100 cycles under limited Li and lean-electrolyte conditions. (March 2021) |

# Summary

- Develop a new polymer–inorganic SEI for Li anodes using RPC rather than a reactive electrolyte. The so-formed SEI enables stable cycling of Li metal batteries under lean electrolyte, limited Li excess and high capacity conditions.

- Novel EAM strategy regulated the uniform Li deposition and efficiently improved the cycling performance of Li metal batteries at low temperature (-15 $^{o}$C).

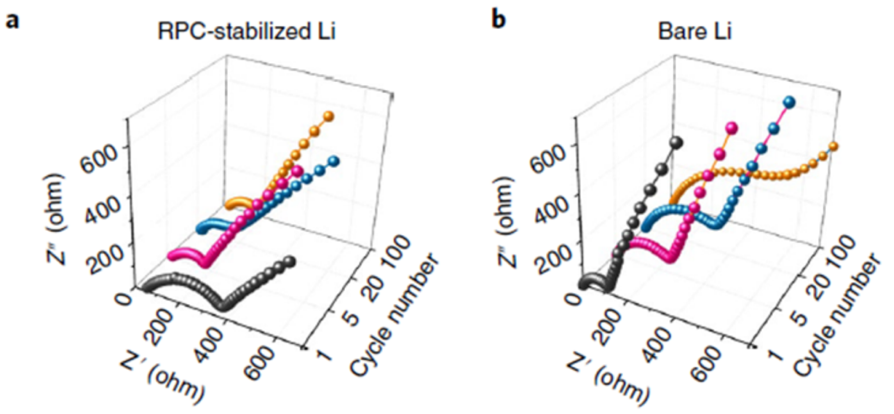
# Acknowledgement

Support from David Howell and Tien Duong at the US Department of Energy’s Office of Vehicle Technologies is greatly appreciated.

# Technical Back-Up Slides

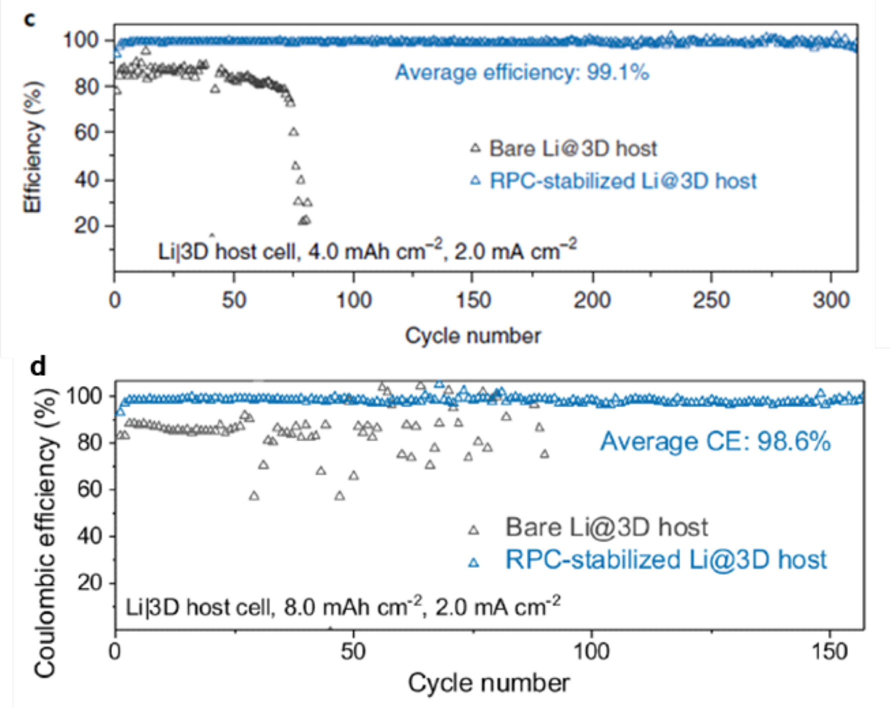
# Interfacial stability of RPC-stabilized Li anodes

**Electrochemical impedance spectroscopy**



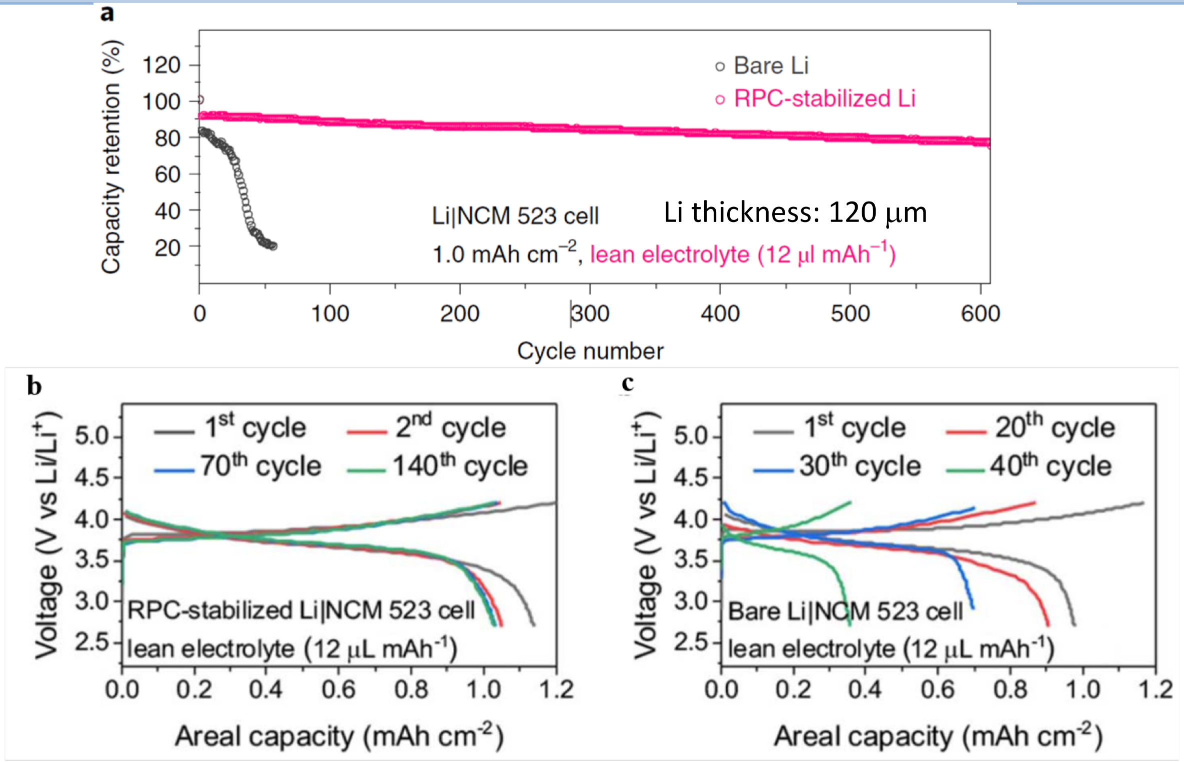

RPC-stabilized Li displays stable resistance, while bare Li increase dramatically .

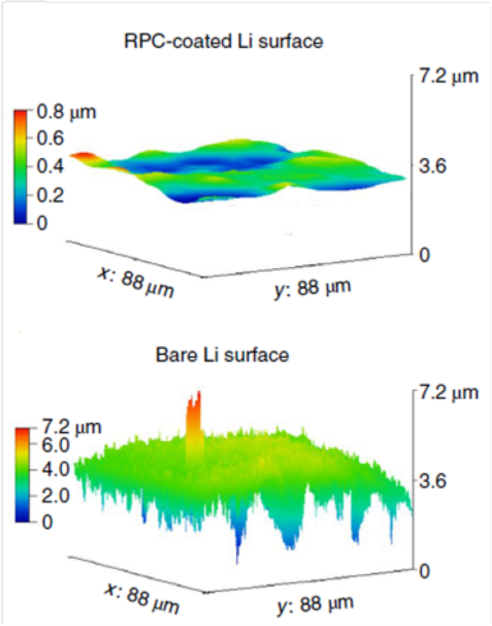
**Li Plating/stripping test**




Efficiency of Li deposition in Li|3D host cells at capacity of 4.0 and 8.0 mAh $cm^{-2}$

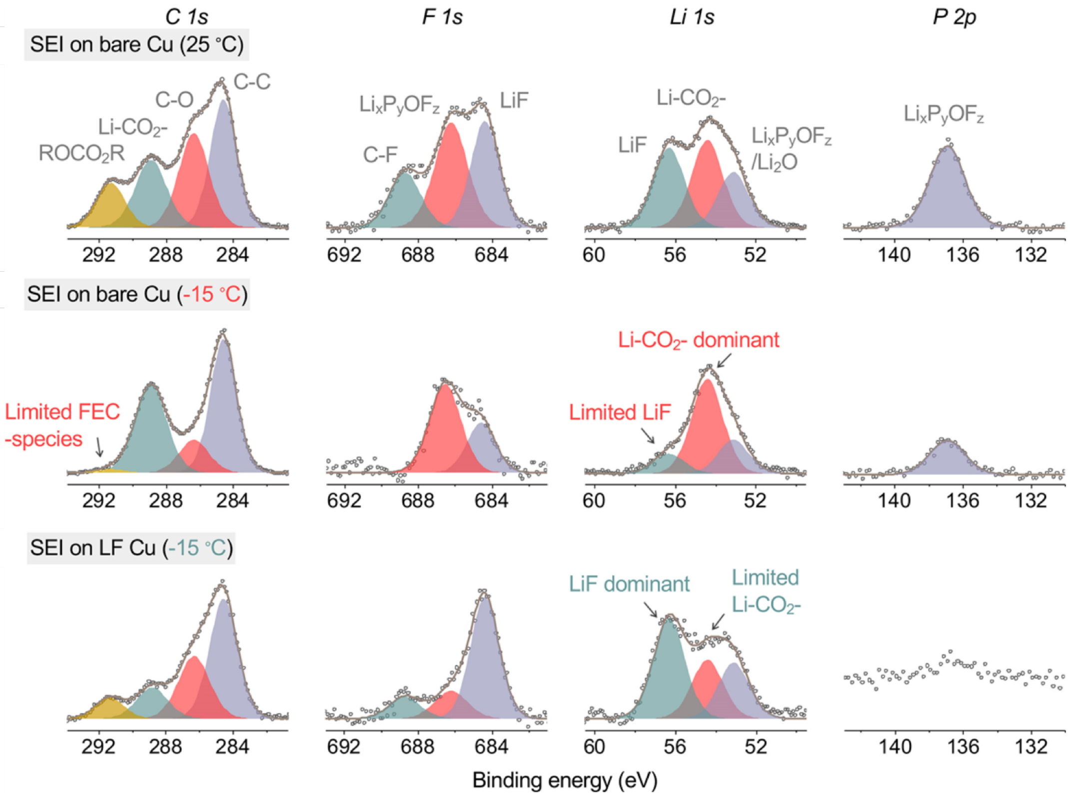
# Cycling performance of RPC-stabilized Li anodes

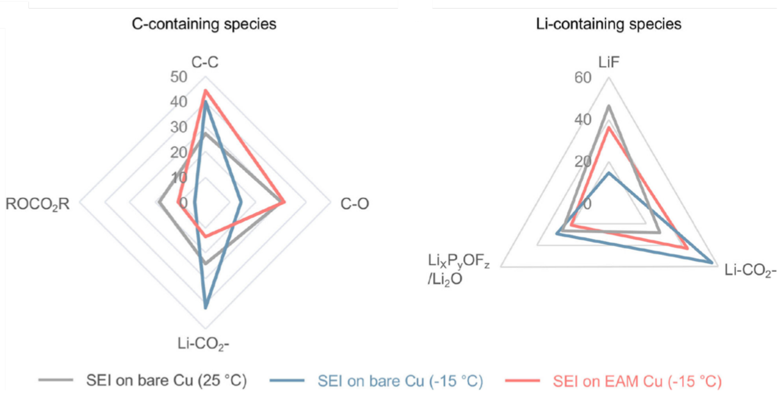



The thin RPC-derived SEI demonstrated improved cycling stability of Li metal batteries under lean electrolyte conditions.

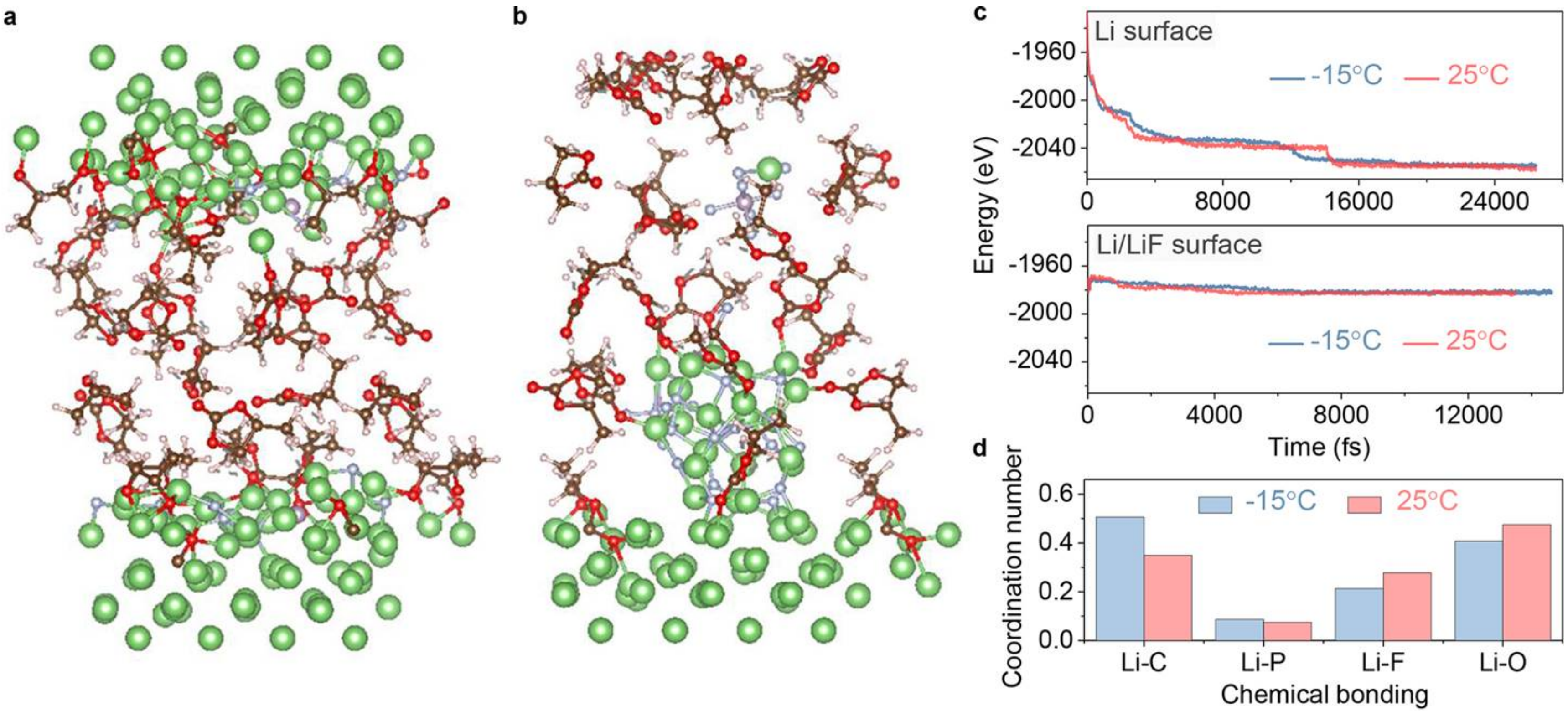
# SEI Chemistry regulated by EAM




The EAM provided a distinct and LiF dominant layer at low temperature (-15 $^{o}$C)

# Interface stabilized by the LiF-rich inner layer




Collaboration with Dr. Anh Ngo from Argonne National Lab.